Lanthanide Tetraphenylimidodiphosphinates: *X*-Ray Structure of an Ethyl Acetate Adduct and Use as N.M.R. Shift Reagents for Acids

I. Rodriguez,[a] C. Alvarez,[a] J. Gomez-Lara,[a] R. A. Toscano,[a] N. Platzer,[b] C. Mulheim,[b] and H. Rudler*[c]

[a] *Institudo de Quimica, Universidad Nacional Autonoma de Mexico, Circuito Exterior, Ciudad Universitaria, Coyoacan 04510, Mexico D.F.*

[b] *Laboratoire de Chimie Structurale, UA 455, Université Pierre et Marie Curie, T 74 4 place Jussieu, 75252 Paris Cedex 5, France*

[c] *Laboratoire de Chimie Organique, UA 408, Université Pierre et Marie Curie, T 74 4 place Jussieu, 75252 Paris Cedex 5, France*

Lanthanum tris(tetraphenylimidodiphosphinate) {La(tpip)$_3$} reacts with ethyl acetate to give a stable 1 : 1 adduct, the *X*-ray structure of which has been established; complexes of the general structure Ln(tpip)$_3$ can be used successfully as n.m.r. shift reagents in association with acids and phenols.

Lanthanide shift reagents have been the subject of much work owing to their ability to effect n.m.r. spectral simplifications.[1—4] However, one of the drawbacks of the commonly used reagents is their sensitivity to water and to acids. We describe here some new lanthanide complexes containing the imidodiphosphinate ligand, and the reaction of the lanthanum complex with ethyl acetate to give a stable, crystalline, heptaco-ordinate complex; we also outline the use of these complexes as new shift reagents especially applicable to phenols and acids.

The Ln^{III} complexes were prepared, free of any external ligand,[5] by addition of stoicheiometric amounts of an aqueous solution of the lanthanide chloride to an aqueous solution of the potassium salt of the ligand. These complexes are very soluble in CHCl$_3$ (*ca.* 400 mg ml^{-1}) and in acetone. Thus an important function of the tpip ligand is to impart extremely high solubility. During attempts to recrystallize the La^{III} complex from ethyl acetate, a new complex containing a co-ordinated molecule of the solvent could be isolated as stable, white crystals, m.p. 226 °C. Crystals suitable for an *X*-ray† analysis could be grown from ethyl acetate. The i.r. (KBr; ν_{CO} 1704 cm^{-1}) and ^{1}H n.m.r. spectra and elemental analysis clearly showed the presence of the co-ordinated ligand.

---

† *Crystal data:* $C_{76}H_{68}LaN_3O_8P_6$, $M = 1476$, triclinic, space group $P1$, $a = 11.006(3)$, $b = 14.053(5)$, $c = 25.736(5)$ Å, $\alpha = 83.88(2)$, $\beta = 81.29(2)$, $\gamma = 67.37(2)°$, $Z = 2$, $D_c = 1.35$ g cm^{-3}, λ (Mo-K_α graphite monochromator) = 0.71069 Å, μ (Mo-K_α) = 7.74 cm^{-1}; 9465 data collected at room temperature with a Nicolet R3 diffractometer. No absorption correction was applied. The structure was solved by standard Patterson-Fourier techniques and refined by least-squares methods using anisotropic temperature factors for all atoms but hydrogen. Hydrogen atoms were placed in calculated positions and were not further refined; they were assigned a fixed overall isotropic thermal parameter. Only 7621 reflections with $|F_0| > 3\sigma\,|F_0|)$ were used to solve and refine the structure to $R = 0.0383$ and $R_w = 0.0506$ $\{w = 1/[\sigma^2\,(F_0) + |0.001|(F_0)^2|]\}$. The program used was SHELXTL. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

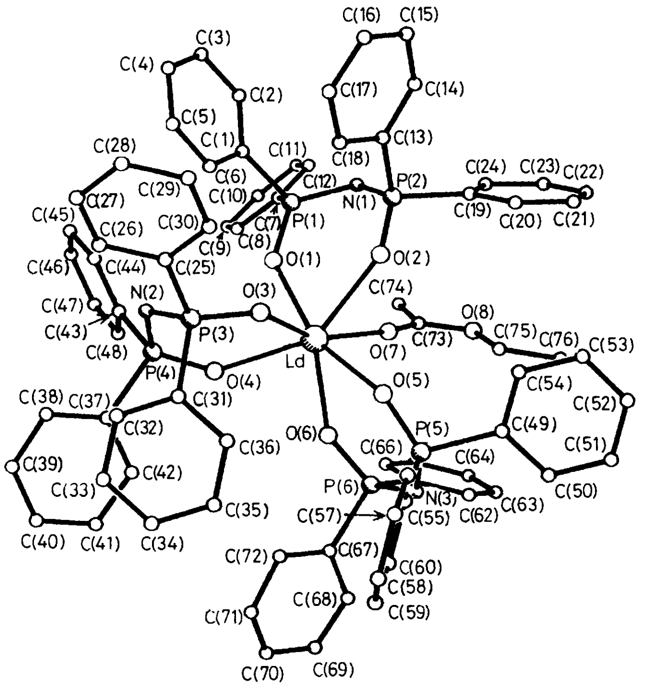

Figure 1. ORTEP view of the lanthanum tris(tetraphenylimidodiphosphonate) ethyl acetate adduct; important bond lengths (Å): La–O(7) 2.587(4), La–O(1) 2.410(4), La–O(2) 2.467(2), C(73)–O(7) 1.184(7), C(73)–O(8) 1.297(7), C(75)–O(8) 1.463(9); important bond angles (°): O(7)–C(73)–O(8) 124.1(7), O(7)–C(73)–C(74) 124.2(6), O(8)–C(73)–C(74) 111.7(5), La–O(7)–C(73) 173.7(4).

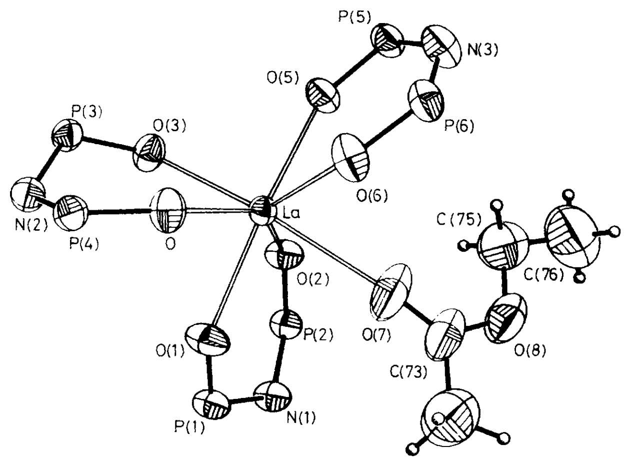

Figure 2. Partial ORTEP view of the ethyl acetate adduct.

An ORTEP view of the ethyl acetate complex is shown in Figure 1, with a partial view in Figure 2. Of special interest are the C=O bond length (1.184 Å) of the co-ordinated ester group as compared with the C=O bond length in a free ester (1.230 Å), and the distance between La and the oxygen atom of the ester group (2.587 Å) as compared with the distance of La to a neutral oxygen atom in other complexes[6,7] (2.58 Å). The geometry of the C=O group of the ester with respect to the metal is also noteworthy. A theoretical study[8] of the geometry of europium ketone complexes concluded that the carbon–oxygen–europium bond angle should be 180°, and in the present case, the angle is 174°, confirming the linearity of the three atom fragment.

The adduct, which is soluble in non-polar solvents, was studied in $CDCl_3$ solution by ^1H n.m.r. spectroscopy: the signals of the ethyl acetate ligand are slightly shifted to high field with respect to those of the free ligand (by 0.18, 0.17, and 0.15 p.p.m. for CH_3, CH_2CH_3, and CH_2CH_3, respectively). Upon addition of ethyl acetate to this solution, a unique set of signals was observed, without broadening. Furthermore, continued addition of ethyl acetate led to progressive shifts of the signals towards those of the free ligand. Thus, an equilibrium is present in solution, and the rate of ligand exchange between free and co-ordinated forms is rapid on the n.m.r. time scale. We therefore reasoned that substitution of the lanthanum cation by a paramagnetic lanthanide cation might provide new shift reagents. Indeed, progressive addition of the praseodymium complex to ethyl acetate, in $CDCl_3$, significantly shifted the signals to high field. The shifts, linearly correlated with the molar ratio of chelate to substrate, were characterized by the slopes (p.p.m. per mol per mol) of 0.50, 0.53, and 0.26 (in the same order as before).

A systematic study of the new chelates with compounds bearing various functional groups showed that the effect decreases in the order carboxylic acids > phenols, alcohols, amines > esters ≫ ketones. By far the most interesting results were obtained with carboxylic acids (*e.g.* $CH_3CH_2CH{=}CHCO_2H$) and phenols (*e.g. p*-nitrophenol). With the praseodymium chelate, the slopes of the linear curves (induced shifts *vs.* molar ratio) reach 14.3 and 5.5 p.p.m. per mol per mol for, respectively, the α-ethylenic proton of the carboxylic acid and the aromatic protons *ortho* to the phenolic function, comparable for example with the slopes observed for conjugated ketones with classical shift reagents.[9]

The sign of the induced shifts is the same for the new reagents as for the β-diketonato chelates, whereas the effectiveness of the new chelates decreases in the order praseodymium > neodymium > europium.

In conclusion, several advantages or complementary properties emerge for the new chelates in comparison with the β-diketonates: the complexing ability of various functional groups towards the two types of chelate is not the same; the narrow area of the spectrum obscured by the signals of the shift reagent ligands is located in the low field region of the proton spectrum; and the reagents are not hygroscopic and not destroyed by carboxylic acids and phenols.

We thank J. C. Daran for discussions.

Received, 30th March 1987; Com. 411

References

1 C. C. Hinckley, *J. Am. Chem. Soc.*, 1969, **91**, 5160.
2 J. K. Sanders and D. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1970, 422.
3 J. Reuben, *Prog. N.M.R. Spectroscopy*, 1975, **9**, 1.
4 O. Hofer, *Top. Stereochem.*, 1976, **9**, 111.
5 I. Rodriguez, C. Alvarez, J. Gomez-Lara, R. Soriano-Garcia, and R. A. Toscano, *Lanthanide-Actinide Res.*, 1986, **1**, 253.
6 A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.
7 B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49.
8 D. G. Raber, C. M. Janks, M. D. Johnston, Jr., and N. K. Raber, *J. Am. Chem. Soc.*, 1980, **102**, 6591.
9 H. Hart and G. M. Love, *Tetrahedron Lett.*, 1971, **7**, 625.